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TECHNICAL REPORT NO. 1

PIEZO- AND PYROELECTRICITY IN POLYMER ELECTRETS

by

M. G. Broadhurst, C. G. Malmberg, F. I. Mopsik and W. P. Harris

Prepared for Publication

in the

Symposium Volume of the Electrochemical
Society - Conference on Electrets, Charge
Storage and Transport in Dielectrics -
Miami Beach, Fla. October 8-13, 1972

Institute for Materials Research, National Bureau of Standards
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ENCLOSURE (2)

PIEZO- AND PYROELECTRICITY IN POLYMER ELECTRETS

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ABSTRACT

A model for a polymer electret, based on an elastically isotropic solid with orientationally frozen molecular dipoles, was developed and tested experimentally. This electret is shown to be both piezoelectric and pyroelectric. The polarization is shown to change with mechanically and thermally induced strains in the polarization direction. The currents generated by the electret will be proportional to the strain rate and, for thin contact electrodes and uniform strains, unaffected by the presence of real charges. Poly (vinyl chloride) films were poled at 80°C, just above their glass transition temperature. The pressure-and temperature-induced short-circuit currents in the polarization direction equalled 0.15(pA/cm^2)/(bar/min) and 2.2 (pA/cm^2)/(K/min) respectively for a specimen poled at 320 kV/cm. These currents were 1) reversible and proportional to the rate of temperature or pressure change, 2) proportional to poling voltage up to 320 kV/cm, 3) in the direction corresponding to increasing polarization with increasing pressure and decreasing temperature, 4) stable with time without special storage conditions, 5) about 1.6 times as great for temperature induced strains as for equivalent pressure induced strains and 6) about 2-4 times as great in magnitude as expected from dielectric constant measurements. The apparent polarization from temperature measurements for the 320 kV/cm specimen was about 1.7 uC/cm^2, or about 1/3 the value expected for maximum alignment of dipoles. In the same specimen the pyroelectric coefficient was found to be $p_3 = -0.39$ nC/cm^2 K and, assuming elastic isotropy, the piezoelectric strain coefficients were found to be $d_{31}=d_{32}=d_{33} = -0.89$ pC/N.

Introduction

Oliver Heaviside first postulated the existence of a permanent electric moment in a dielectric solid [1]. Experimental confirmation came in the early 1920's with the work of Eguchi on wax and rosin mixtures which were solidified in the presence of a strong electric field [2]. It was recognized early [3], that two types of polarization were generally present in electrets - one due to a homocharge having the same polarity, the other due to a heterocharge having the opposite polarity to that of the adjacent polarizing electrode. It is generally agreed that the heterocharge arises from a more or less uniform volume polarization of the dielectric by means of a permanent dipole orientation, by charge diffusion, or by a not-yet-understood charge separation and trapping mechanism. The homocharge is thought to be real charge very near the dielectric surface and due to conduction between dielectric and electrode, to field emission to or from the electrodes, or to breakdown in the electrode-specimen gap. Contact electrification (due to rubbing the surface of the specimen) is also a known source of surface charge.

Soon after their discovery, electrets were shown to be both piezoelectric and pyroelectric [4]. However, work on these effects focused on crystalline solids and little work was done on amorphous electrets. In 1960 Gubkin [5] published an electrostatic theory of piezoelectricity which did not involve the microscopic structure of the electret. This approach would seem to be a much better description of the phenomenon of piezoelectricity in polymer materials, many of which are partially or completely amorphous, than the classical approach [6] which is concerned with structure in the dielectric. Fukada and coworkers [7] have reported results of a large number of measurements of piezoelectricity in biological and synthetic polymers and have emphasized the importance of structure in interpreting the data. Other investigators have reported measurements of piezoelectricity [8,9] and pyroelectricity [9,10,11,12] in poly(vinylidene fluoride) (PVF2) films. The pyroelectric activity in polymers seems to be closely related to piezoelectric activity, and PVF2 is one of the most active of the polymers yet studied. As yet there seems to be no systematic experimental approach to piezoelectric polymers based on bulk theory such as that proposed by Gubkin. Below we give a brief summary of Gubkin's theory and apply it to the piezo- and pyroelectric effects in poly(vinyl chloride) (PVC) films.

Gubkin's Phenomenological Theory

Consider the dielectric-electrode assembly in figure 1. Assume the thicknesses of the disk, L, and air gaps, ℓ, are small with respect to their widths so that edge effects are negligible. The dielectric disk has a dielectric constant κ' and an arbitrary charge distribution $\rho(z)$ assumed to be a function only of the coordinate (z) perpendicular to the disk surface. $\rho(z)$ is made up of both real, $\rho_r(z)$, and induced $\rho_f(z)$ charges and the polarization is given by

$$\text{div } P(z) = -\rho_f(z) \tag{1}$$

Taking a very simple case of no net charge on the disk (i. e. $\int_0^L \rho_r(z)\,dz=0$) and of charges on the opposite surfaces of the disk equal in magnitude but opposite in sign, one can write the surface charge density on the electrodes as

$$\sigma = \left[\frac{\varepsilon_o \kappa' V}{L} - (\sigma_r - P_s)\right]\left(1 + \frac{2\kappa'\ell}{L}\right)^{-1} , \tag{2}$$

where σ_r is the apparent real surface charge due to $\rho_r(z)$, V is the potential difference between the electrodes, ε_o is the permittivity of free space, P_s is the frozen-in part of the (uniform) polarization and σ_r is the real surface charge density [13]. Gubkin [5] identified the piezoelectric effect with the pressure derivative of the electrode surface charge density, $d\sigma/dp$. We will be concerned with the response to both hydrostatic pressure and temperature, θ . The above equation is equivalent but simpler for our purposes than that derived by Hayakawa and Wada [14].

Application to Isotropic Amorphous Solids With Rigid Dipoles

Since we will restrict our measurements to a specific set of experimental conditions, we can simplify Eq. (2). These conditions are:

1) We measure changes in surface charge at nearly zero potential (V=0).

2) We use thin evaporated metal electrodes so that $\ell/L \ll 1$, and the electrodes change area in accord with changes in specimen area, A.

3) We consider only amorphous specimens which we assume to be elastically isotropic.

4) We assume the free charges to be frozen in the solid and to move in proportion to macroscopic strains, and the polarization charges to be rigid molecular dipoles whose positions move in proportion to macroscopic strains but whose effective total moment, M, remains constant as long as the strains are isotropic.

Under these conditions, with $\sigma_r = Q_r/A$ and $P_s = M/AL$, we can write the electrode charge as,

$$Q = -Q_r + M/L. \tag{3}$$

We will use a coordinate system fixed in the specimen such that the + z axis is normal to the film surface in the direction of the poling field and x and y are in the plane of the film. The charge, Q, is that on the surface which was maintained at a positive potential during poling (bottom electrode in figure 1). The electrode charge depends only on sample thickness, L, and will change with isotropic volume strain $d(\ln v)$ according to

$$\partial Q/\partial(\ln v) = -A\,P_s/3. \tag{4}$$

The pressure (p) and temperature (θ) dependence of the electrode charge are given by,

$$(\partial Q/\partial p)_{V=0,\theta} = A\,P_s\beta/3, \tag{5a}$$

and

$$(\partial Q/\partial \theta)_{V=0,p} = -A\,P_s\alpha/3, \tag{5b}$$

and the currents from this electrode resulting from a varying pressure or temperature are given by

$$I_{V=0,\theta} = -P_s\,A\,\beta(dp/dt)/3, \tag{6a}$$

and

$$I_{V=0,p} = P_s\,A\,\alpha(d\theta/dt)/3. \tag{6b}$$

In the above $\alpha = (\partial(\ln v)/\partial\theta)_p$ is the coefficient of thermal expansion and $\beta = - (\partial(\ln v)/\partial p)_\theta$ is the compressibility, and V=0 means at constant near-zero voltage.

The piezoelectric strain coefficient $d_{ij} = (\partial P_{si}/\partial T_j)_V$ is the change in the polarization along the i direction with respect to stress T_j at constant electric field. Thus, for the elastically isotropic electret

$$d_{3j} = - P_s (\partial \ln v/\partial T_j)_V = - P_s \beta/3 \tag{7}$$

$$d_{31} = d_{32} = d_{33} = - (\partial Q/\partial p)_{V=0,\theta}/A. \tag{8}$$

The pyroelectric coefficient at zero field $p_i=(\partial P_s/\partial\theta)_T$ is the change in polarization at constant stress along the i axis with respect to temperature. Thus,

$$p_3 = - P_s(\partial \ln v/\partial\theta)_T = - P_s\alpha = 3(\partial Q/\partial\theta)_{V=0,p}/A. \tag{9}$$

One can estimate the expected value of P_s during poling from dielectric constant data. If at room temperature the static dielectric constant is κ'_R and at some elevated temperature, from which the sample is cooled under an applied field, E_{pole}, the dielectric constant is κ'_θ, then the poling procedure can be expected to freeze in a dipolar polarization

$$P_p = (\kappa'_\theta - \kappa'_R)\varepsilon_o E_{pole} . \tag{10}$$

In general, for a non-crystalline polar material like PVC, P_p is considerably less than the maximum value of P possible by complete dipole alignment, and is usually linear with E_{pole} up to breakdown fields. Crystalline materials such as PVF2 are reported capable of a much higher degree of orientation than PVC [15]. It is convenient to use a reduced polarization $P_s/\varepsilon_o E_{pole}$ to describe a particular polymer. This quantity gives the apparent freezeable dielectric increment and is comparable to the reduced heterocharge used to describe thermally stimulated current results [16].

Specimens

The specimens used in this study were made from 5 mil (127 μm) commercial rigid PVC film with a glass transition near 70°C. The material was quite stable with respect to weight loss, as determined by repeated weighings after temperature cycling and evacuation. After the films were cleaned with detergent and water and dried, circular gold electrodes of 6.35 cm^2 area were evaporated on both sides of each specimen. Some measurements were also made on a commercial film of PVF2.

Poling

Specimens were placed between 1/4" thick glass plates to prevent distortion and heated to (80 ± 1)°C in an oven. A high voltage DC power supply was used to apply (3.9 ± 0.2) kV across a series of wire-wound resistors (with ± 1% nominal accuracy) having a total of 9.6 MΩ resistance. These resistors were arranged so that taps were available at 1/2, 1/4, 1/8 and 1/96 of the total resistance. These resistance ratios had a measured accuracy of better than ± 1%. The taps were used to apply voltages of 3.9, 3.9/2, 3.9/4 and 3.9/8 kV across specimens A1, A2, A3 and A4 respectively. The voltage from ground to the 1/96 total resistance tap was monitored with a precision voltmeter and recorder.

Immediately following application of the poling voltage the oven was cooled from 80°C to room temperature in 1/2 hour. During this time the poling voltage gradually increased by about 2%.

Specimen B1 (PVF2) was poled under similar conditions.

Measurements of Piezo- and Pyroelectric Currents

The specimen holder shown in figure 2 was machined from solid copper 10.2 cm in diameter and 8.9 cm high. The specimen chamber is 5.1 cm in diameter and 3.2 cm high. (A minimum of 2.5 cm wall thickness surrounds the chamber). One thermocouple hole is located in the copper just below the center of the chamber and pressure-tight fittings are used to admit a second thermocouple and a shielded current-measuring lead to the chamber. A copper tube in the lid allows helium gas to be added to and removed from the chamber and the lid is sealed with a rubber "O" ring and secured with cap screws. Pressure is controlled by allowing helium gas

from a cylinder to leak into and out of the chamber through a metering valve and is monitored with an accuracy of better than ± 1% with a pressure transducer and strip-chart recorder (all shown in figure 3).

To change and control its temperature, the holder is placed on the copper block shown in figure 3. Streams of warm and cool water from thermostated baths pass through the block, and the rate of heating and cooling is controlled by the positions of the valves shown in figure 3. The temperatures in the block and chamber are measured with a precision voltmeter and monitored on a chart recorder. A double chromel-constantan thermocouple in the chamber gives an emf of 120 μV/K. The holder is conveniently used up to 14 bar (200 psi) and within ± 10 K of room temperature.

The poled specimens are placed in the bottom of the chamber with the "plus" electrode up. The "plus" electrode is the one maintained at positive potential during poling. A specimen is in place in figure 2. The specimen's bottom electrode is in contact with the grounded copper can. A spring and foam sponge provide the force necessary to maintain contact between the upper specimen electrode and a thin brass strip connected to the shielded current-measuring lead. This lead is connected to a low-impedance current amplifier which is specified to operate with a maximum of 400 μV across the input leads. The current amplifier is operated on a (10^{11} ± 4%)V/A range and the amplifier output drives a strip-chart recorder with a calibrated (± 1%) full scale sensitivity of from 100 to 0.01 V. The chart recorder is typically used to measure 10^{-11} A full scale, with a nominal accuracy of ± 5%.

Pressure, temperature and current data are recorded simultaneously on chart recorders and are then analyzed by measuring from the chart records several values of the slopes of the pressure-time curves and corresponding currents at constant temperature and of the temperature-time slopes and corresponding currents at constant pressure. Data taken in this way from a single specimen loading yield a standard deviation of ± 2%. Values for different loadings of the same specimen show a variation of about 5%. Including uncertainties in specimen thickness, electrode area, time, poling voltage, etc.,we found the precision to be about 5% and estimated the accuracy to be about 10%.

Typical Data

Strip chart recording traces for specimen A1 are shown in figures 4 and 5. In figure 4 the specimen is first cooled, heated and cooled again in the region of 23°C. The magnitude of the current increases as the rate of temperature change, $d\theta/dt$, increases, reverses with a reverse in temperature change and is constant when $d\theta/dt$ is constant and zero when $d\theta/dt$ is zero. Cooling produces a negative current from the "plus" electrode. Figure 5 shows the results of increasing and decreasing the pressure through two cycles around 120 psi (about 8 bars). Here the current response is more complex because of adiabatic temperature effects in the helium pressurizing gas during pressure change. As the metering valve is opened the helium enters the chamber causing a piezoelectric response. Heating by the gas causes an opposite pyroelectric response which gradually diminishes as the specimen temperature equilibrates (in about 30 s). The piezoelectric current then predominates and gradually decreases in magnitude as the rate of pressure change falls off and the pressure approaches the fixed pressure head. The direction of the piezoelectric current is such that an increase in pressure produces a negative current from the "plus" electrode. The polarization of the sample thus increases with either a decrease in temperature or an increase in pressure as expected from the electret model.

Results of the Measurement

The results of the measurements are shown in Table 1. The values of $P_s(p)$ and $P_s(\theta)$ were calculated from Eq. (6) using values of $\beta/3 = 0.86 \times 10^{-5}$/bar and $\alpha/3 = 0.78 \times 10^{-4}$ /K which we measured for one of the PVC films in the z direction with a capacitive strain gauge to be described elsewhere. These values are in reasonable accord with published values for bulk PVC of $\beta/3 = 0.80 \times 10^{-5}$/bar and $\alpha/3 = 0.67 \times 10^{-4}$/K [17], indicating that large anisotropic effects are not present. Assuming isotropy we can reduce the piezoelectric results further with the aid of Eq. (8). Values of the piezoelectric strain constants so calculated are shown in Table 2, with some values chosen from the literature for other materials.

The pyroelectric coefficients, p_3, of PVC are proportional to the poling field from 320 to 40 kV/cm. The values obtained are about $p_3 = 1.2 \times E_{pole}$ nC/cm^2 where E_{pole} is in MV/cm. These values are quite comparable to reported values of 0.3 - 2.4 nC/cm^{2}K for PVF2 films poled at 1 MV/cm. The pyroelectric coefficients in Table 1 showed no indication of decay after 6 weeks for the A series of PVC samples nor after 4 months for some comparable specimens prepared earlier.

Discussion of the Results

The apparent reduced polarization of the A specimens of PVC from Table 1 is 61.8 from temperature measurements and 38.3 from pressure measurements. Dielectric constant data [21] indicate that cooling from 80°C to room temperature under an applied field should yield a reduced polarization of only about 10. Measurements on the PVC used in this study gave essentially the same result. It is not clear where the extra apparent polarization comes from or why the temperature and pressure data yield different values. Very slow cooling near 80°C would allow more polarization as shown by Reddish [21] because of the gradual stiffening of the polymer chain just above the glass transition temperature. However, it is difficult to see from Reddish's data how this effect could give a reduced polarization greater than about 15. Another possible source of the enhanced polarization is anisotropic thermal expansion and compressibility in the films which might allow the dipoles to tilt during strain. A third possibility is that some as-yet-not-understood charge separation - trapping mechanism sometimes proposed for electrets [22] enhances the polarization. A reduced heterocharge of 16.1 has been reported from TSD measurements on PVC [16], in agreement with the value expected from dielectric data.

If one calculates the maximum polarization possible in PVC assuming complete dipole alignment one finds, with a dipole moment of 3.6×10^{-30} C·m (1.1 Debye) per repeat unit and a density of 1.4 g/cm^3 [21], a P_{max} of 5×10^{-6} C/cm^2 . This value is roughly triple the apparent polarization from temperature data for the A1 specimen. If specimen A1 is at one third maximum dipole alignment, non-linear effects due to saturation would still be within experimental error in our measurements.

Conclusions

The piezo- and pyroelectric currents generated in PVC films due to changing temperature and pressure are found to be quite stable, reproducible and well behaved. The measured effects are accounted for quite well by a model of a simple elastic solid with partially ordered rigid dipoles. These results indicate that this model is a good basis for understanding and studying piezo- and pyroelectric effects in polymers.

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Table 1. Summary of Piezo- and Pyroelectric Data on PVC

Specimen	E_{pole} (kV/cm)	p_3 (nC/cm^{2}K)	$d_{31}=d_{32}=d_{33}$ (pC/N)	P_s μC/cm^2 from T	from p	$P_s/\varepsilon_o E_{pole}$ from T	from p
A1	320	−0.402	−0.873	1.72	1.02	60.6	35.8
A1 (repeat after 2 weeks)	320	−0.384	−0.909	1.64	1.05	57.9	37.3
A2	160	−0.214	−0.510	0.912	0.593	64.4	41.9
A3	80	−0.104	−0.244	0.445	0.284	62.8	40.0
A3 (inverted)	80	−0.100		0.428		60.4	
A4	40	−0.0537	−0.111	0.229	0.129	64.8	36.4
B1 (PVF2)	320	−0.885	−0.704				
			Average for PVC samples			61.8	38.3

Table 2. Piezoelectric Strain Coefficients

Material	E_{pole} (kV/cm)	d_{31} (pC/N)	d_{33} (pC/N)	Reference
PVC	$E_p<320$	$-0.93\ E_p/320$	$-0.93\ E_p/320$	this work
PVC	180	0.3-0.5		8
PVC		11-80		18
PVF	200	1-1.3		8
PVF2	320	3-7		8
PVF2	300	2		19
BeO		−0.12	0.24	20
ZnO		−4.7	12	20
CdS		−5.18	10.32	20
CdSe		−3.92	7.84	20
$BaTiO_3$		−34.5	85.6	20

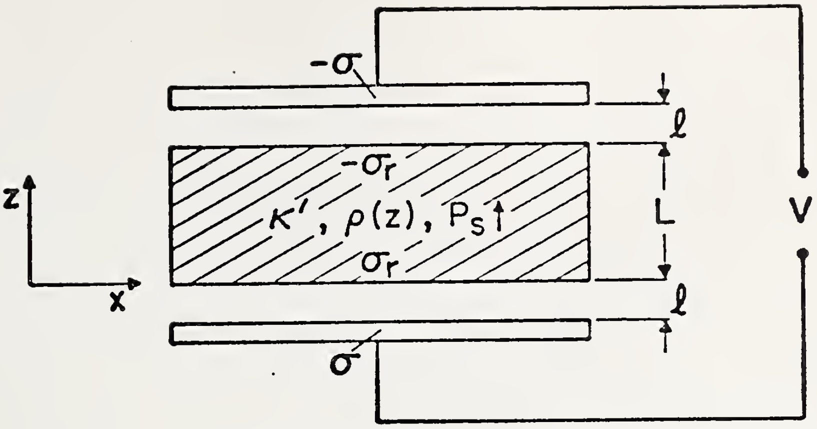


Figure 1. Specimen electrode arrangement.

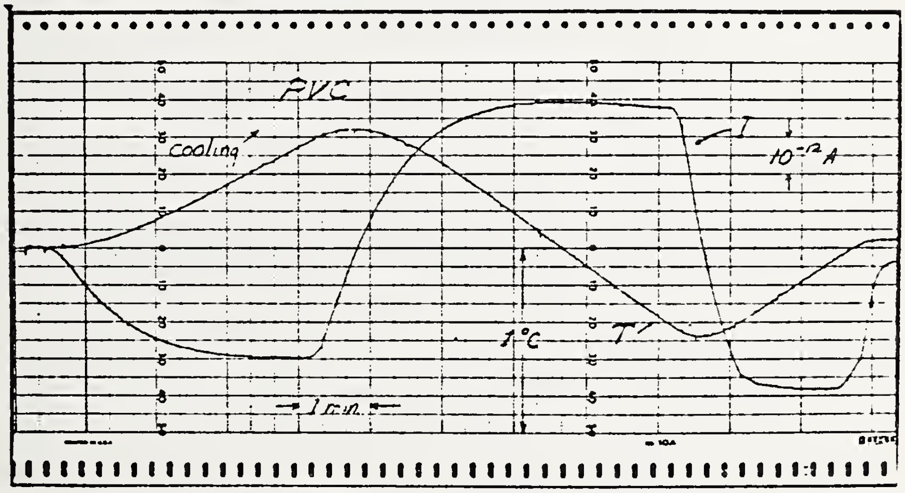


Figure 4. Temperature and current for PVC specimen A1 poled at 320 kV/cm. Cooling produced a negative current from the "plus" electrode.

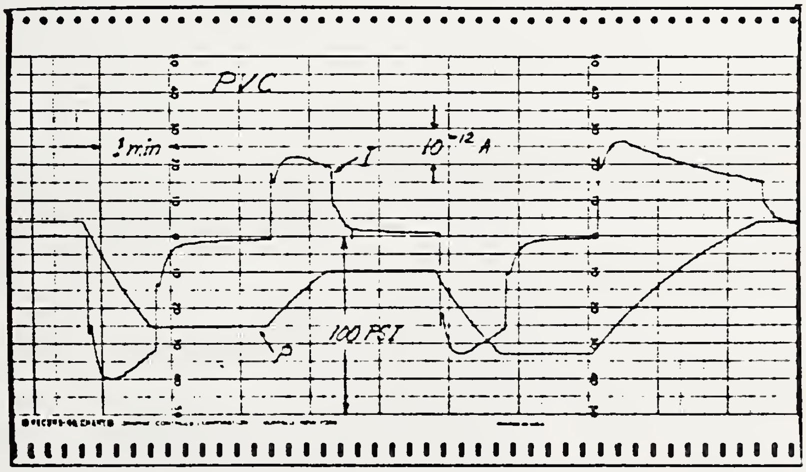


Figure 5. Pressure and current for PVC specimen A1 poled at 320 kV/cm. Pressurizing produced a negative current from the "plus" electrode.

Figure 2. Specimen holder showing specimen in place in bottom of chamber.

Figure 3. Specimen holder, pressure and temperature control devices and current measuring and recording equipment.

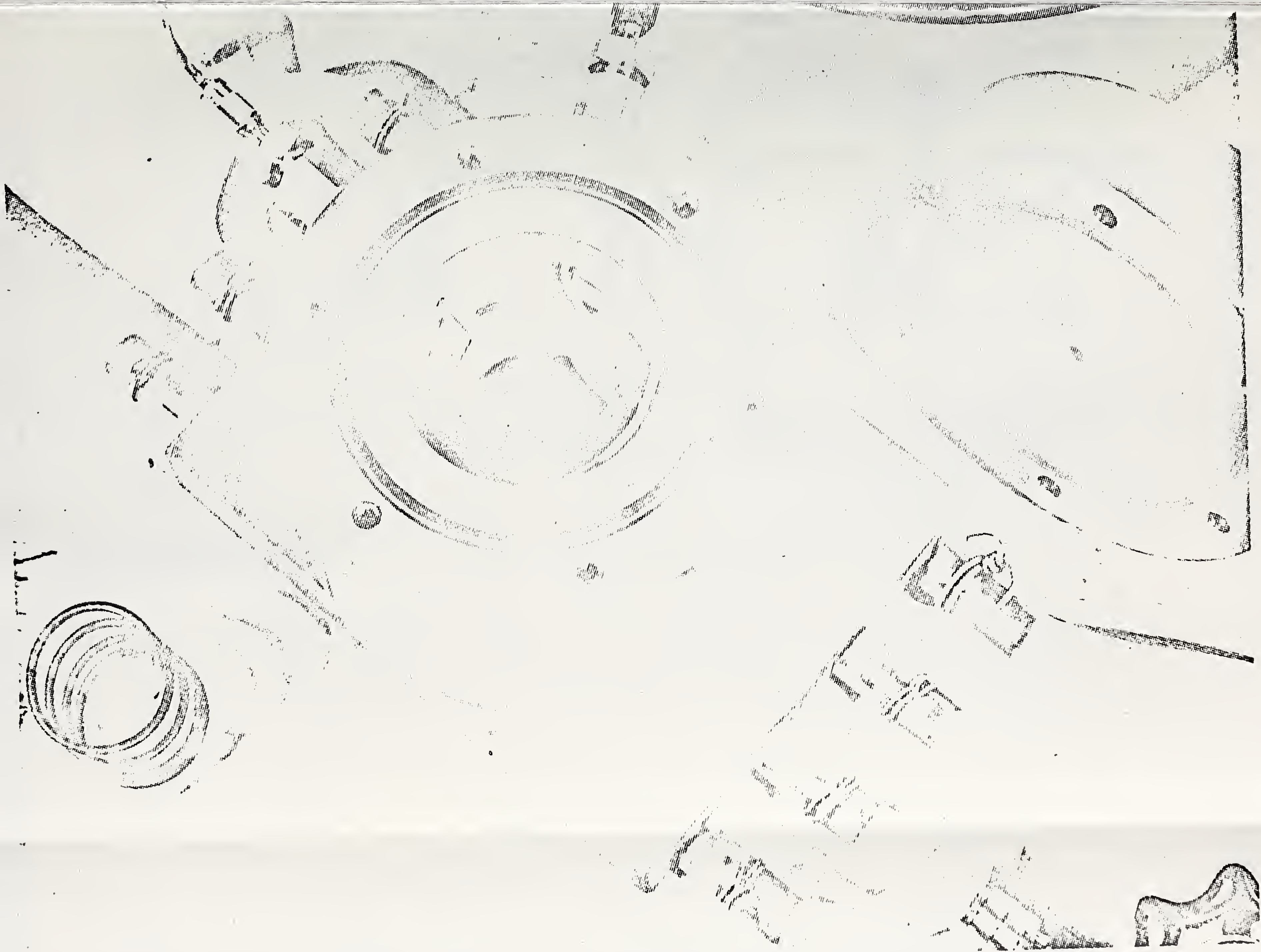
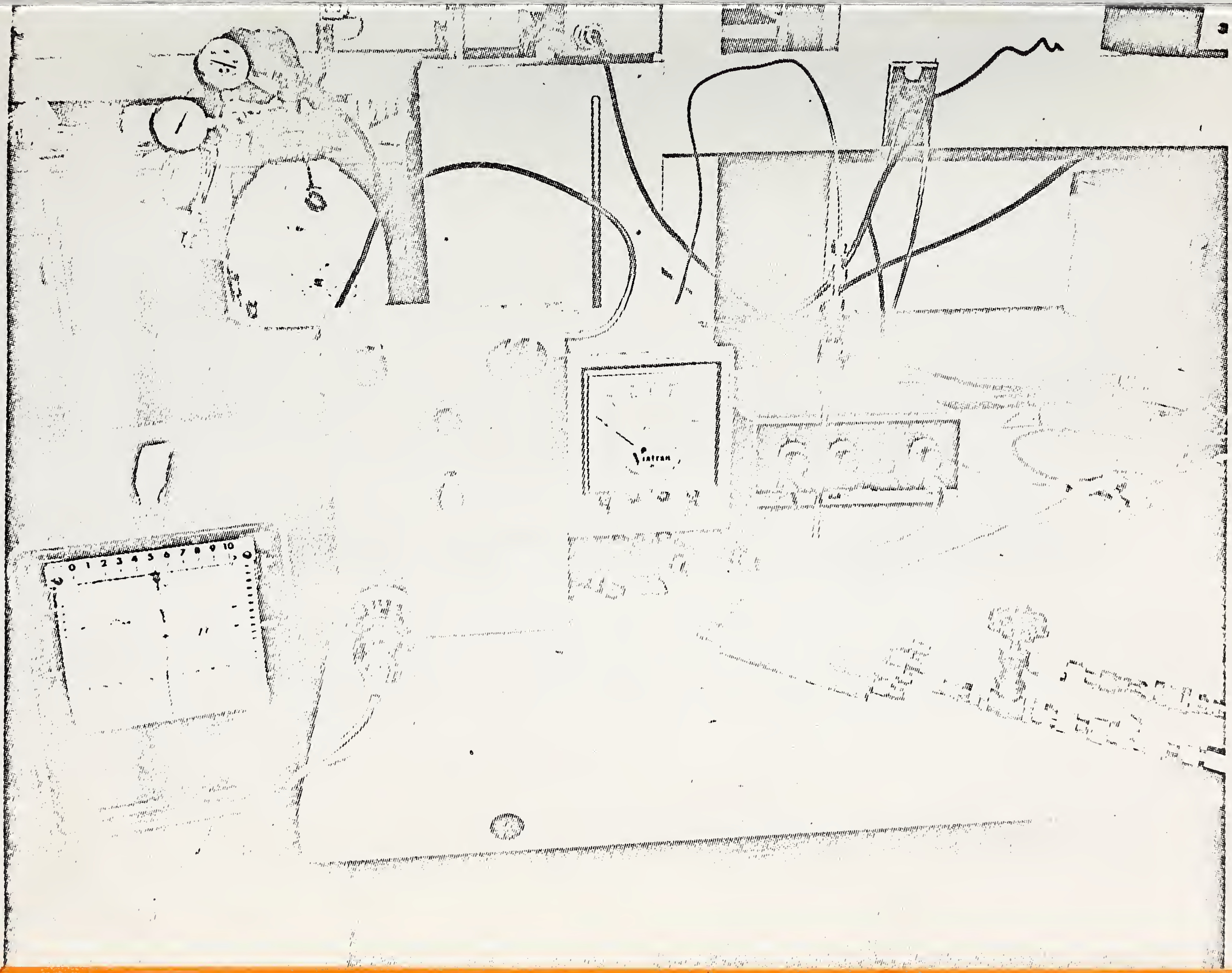


Fig 2



0 1 2 3 4 5 6 7 8 9 10
Vintran